Analytical Green Star Area (AGSA) as a new assessment tool for electrochemical determination of cyclobenzaprine hydrochloride in wastewater sample using Recycled graphite modified nitrogen-doped CQDs

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2. Experimental

Instruments

The samples were examined as 1.5% KBr pellets by Infrared spectra and recorded on FTIR Nicolet 5 DX Spectrophotometer at the National Research Center in The Dokki district of Cairo. SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Ana-lyzes), with accelerating voltage 30 K.V., Thermo Fisher Scientific (FEI) Company, at the National Research Center in The Dokki district of Cairo – Egypt. The X-ray diffraction (XRD) analysis was employed (with Cu-Ka radiation = 0.15406 nm wavelength) using a SIEMENS D5000 X-ray diffractometer. With a resolution of 0.05, the diffraction data were obtained for 2θ between 10° and 80° at room temperature for nitrogen doped CQDs at Central Metallurgical Research & Development Institute. Transmission Electron Microscope (TEM) (JEM-2100 electron microscope operated at 200 KV and resolution = 0,2 nm (JEOL Ltd., Tokyo, Japan). The examination carried out at the National Research Center in The Dokki district of Cairo – Egypt. Potentiometric measurements were performed using JENWAY 3510 pH/mV meter (Staffordshire, UK) where all measurements were conducted with a commercial Ag/AgCl double junction reference electrode (Thermo Scientific Orion, USA). PalmSens4, The Netherlands using PSTrace 5.11 software for activation of recycled graphite waste electrode. Molecular operating environment (MOE®, 2014) was used in building 3D structures for molecular docking.

Materials, reagents, and solutions:

All chemicals and solvents of analytical grade were used. Egypt). Pure powder of 99.55% cyclobenzaprine was obtained Global Napi Pharmaceutical Company, 6-October City, Egypt. Moveasy® tablets (10 mg/tablet), were purchased from a local Pharmacy. Paracetamol standard with claimed purity of 99.76% was obtained from SIGMA pharmaceutical industries, Cairo, Egypt. Pure Diclofenac sodium (99.73%) was kindly provided by EIPICO Company, 10th of Ramadan City, Cairo, Egypt.

high molecular weight polyvinyl chloride (PVC), Tetrahydrofuran (THF), sodium hydroxide, magnesium stearate, sucrose, glucose, NaCl, $CaCl_2$, urea, starch, KCl and NH_4Cl were purchased from El-Nasr Co. L-Serine, Sodium tetraphenyl borate (NaTPB), ammonium reineckate (RK), tetrapentyl bromide, dibutyl phthalate (DBP), Tributyl Phosphate(TBP) dioctyl phthalate (DOP) and β-Cyclodextrin (β-CD) alpha dextrin (α-CD) and gamma cyclodextrin (γ-CD) were (extra pure AR, ACS, 98%) from SRL company were provided by Sigma Aldrich, Germany. 0.04 M Britton-Robinson buffer (BR buffer) was prepared from 0.04 M boric acid (99.8%, Polski EODZNN Chemiczne S.A. Co., Poland), 0.04 M phosphoric acid (85%, Adwic Co., Egypt) and 0.04 M acetic acid (99.7%- Loba- Chemic Co., India), the pH was adjusted in the range 2 -9 with 0.2 M NaOH (98%, Adwia Co., Egypt).

Table (S1) effect of different electrode composition on electrode performance.

plasticizer	ionophore	Cationic exchanger	Modifier	Linearity range (M)	Slope response (mV/decade)
TBP	-------	TPB	NCQDs	1.0×10^{-3}- 1.0×10^{-5}	50.2
TBP	-------	RK	NCQDs	1.0×10^{-3}- 1.0×10^{-5}	49.56
TBP	α-CD	TPB	NCQDs	1.0×10^{-2}- 1.0×10^{-6}	51.20
DBP	-------	TPB	-------	1.0×10^{-3}- 1.0×10^{-5}	45.87
DBP	-------	TPB	NCQDs	1.0×10^{-2}- 1.0×10^{-5}	48.45
DBP	α-CD	TPB	NCQDs	1.0×10^{-2}- 1.0×10^{-6}	47.45
DOP	-------	TPB	-------	1.0×10^{-3}- 1.0×10^{-5}	-56.00
DOP	-------	TPB	NCQDs	1.0×10^{-2}- 1.0×10^{-5}	-51.4
*DOP	α-CD	TPB	NCQDs	1.0×10^{-2}- 1.0×10^{-7}	-57.97
DOP	β-CD	TPB	NCQDs	1.0×10^{-2}- 1.0×10^{-6}	-55.60
DOP	γ-CD	TPB	NCQDs	1.0×10^{-2}- 1.0×10^{-6}	-55.3

*The optimized chosen sensor for CBZ determination.

Table 2S. The twelve foundational principles established by the GAC, along with the evaluative framework associated with each principle as delineated by the AGSA metric.

principle	**Method metrics**
Principle 1: What is the extent of sample treatment required before analysis?	Moderate treatment (pH adjustment)
Principle 2: What is the sample size required for the analysis?	>1gm
Principle 3: Where are the measurements performed?	Samples are analyzed in field lab
Principle 4: What is the level of integration of analytical processes?	Some processes integrated, reducing step and instrument use
Principle 5: What is the degree of automation and miniaturization of the method?	Semi-automated and semi-miniaturized
Principle 6: Does the method require derivatization?	No derivatization
Principle 7: What is the volume of waste generated by the method? How is analytical waste managed in the method?	Less than 100 mL per sample
Principle 8: How many analytes are determined by the method in a single run?	One sample
Principle 9: What is the amount of energy consumed by the analytical process?	< 0.1 KW/sample
Principle 10: What is the source of reagents used in the method?	Renewable green reagents
Principle 11: What is the hazard level of reagents used in the method?	2 pictogram or less
Principle 12: What level of safety is provided for the operator during the procedure?	Low risk procedure
Total score	**77.78**

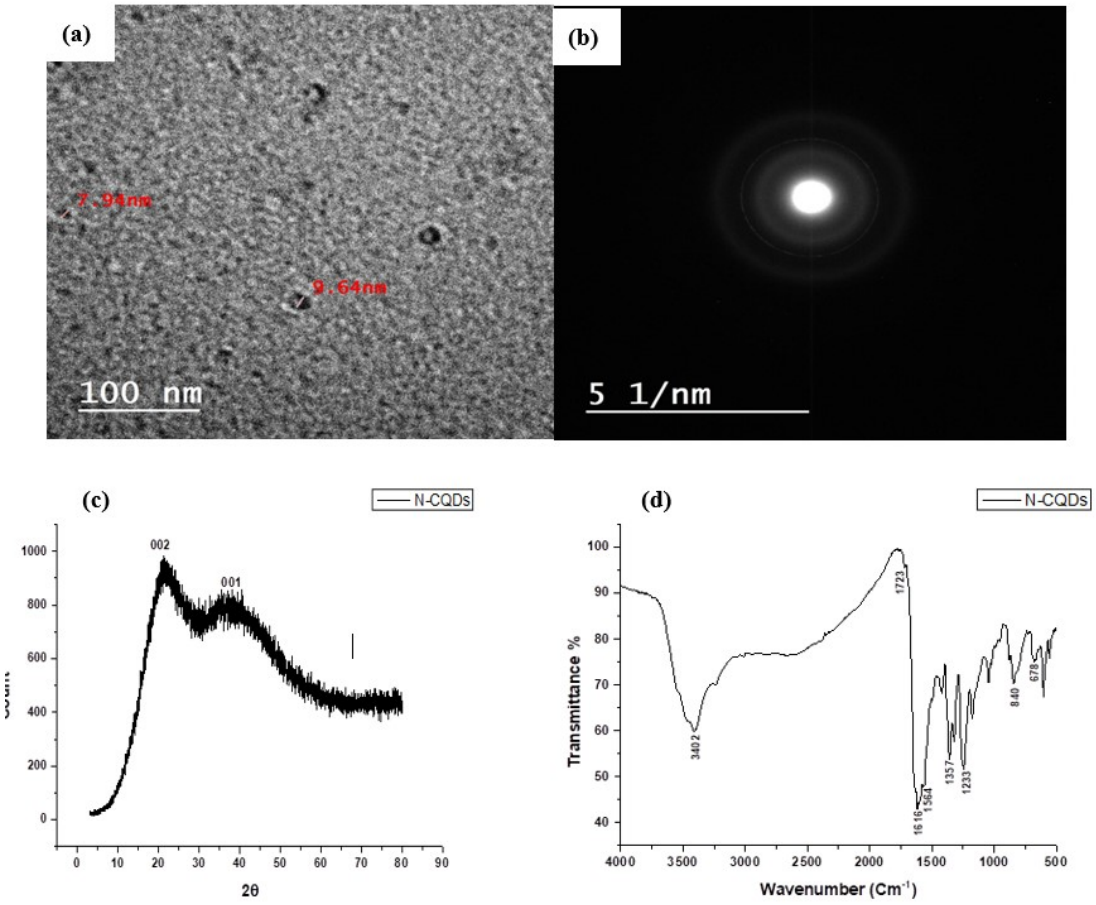

Figure S1: (a) TEM image of PP-NCQDs, (b) SAED for PP-NCQDs, (c) XRD spectrum for PP-NCQDs and (d) FTIR of PP-NCQDs.

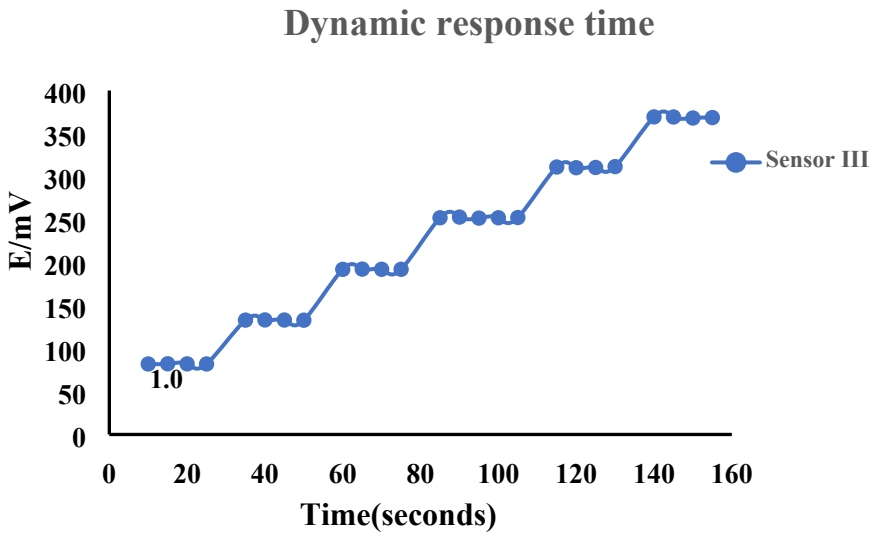

Figure S2: Dynamic response time for the proposed sensors III according to their different linearity range.

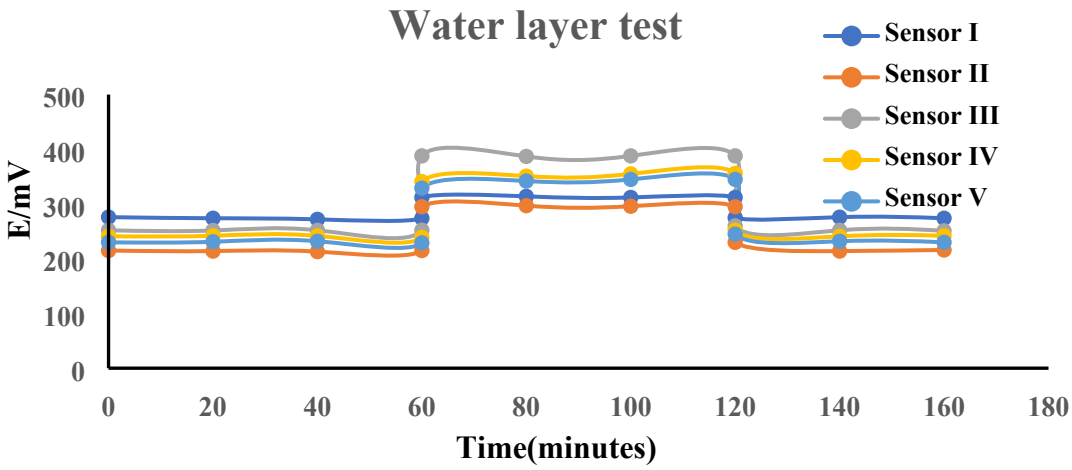

Figure S3. Potentiometric water layer test for all utilized sensor.

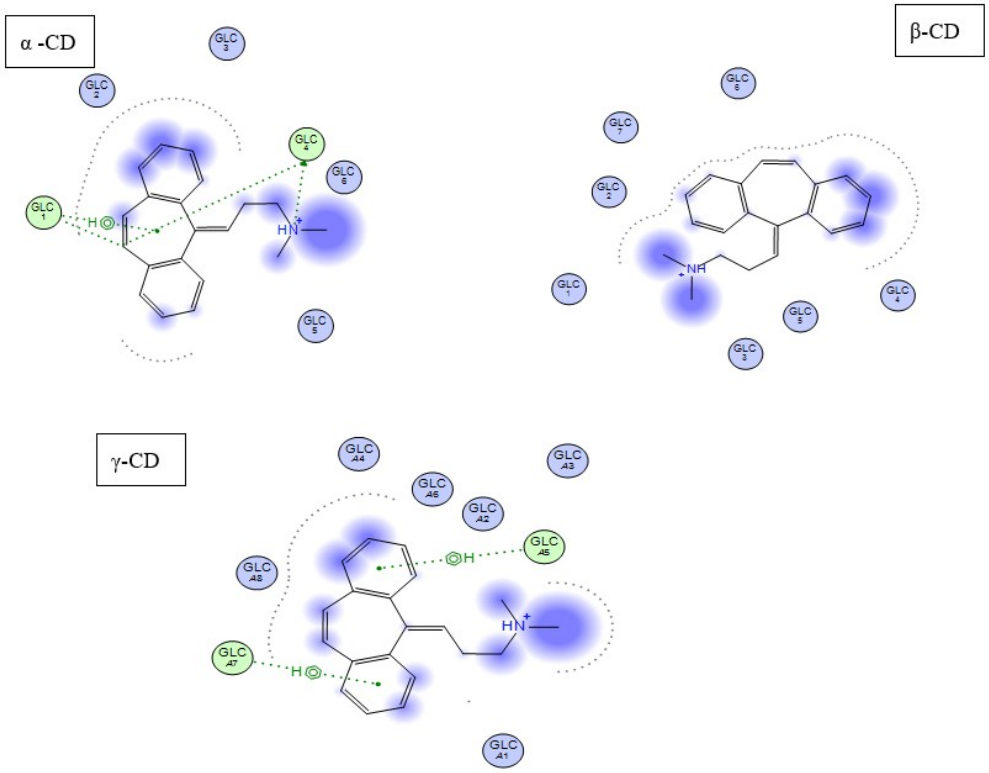

Figure S4: Displayed 2D binding sites interaction between different ionophores and CBZ.

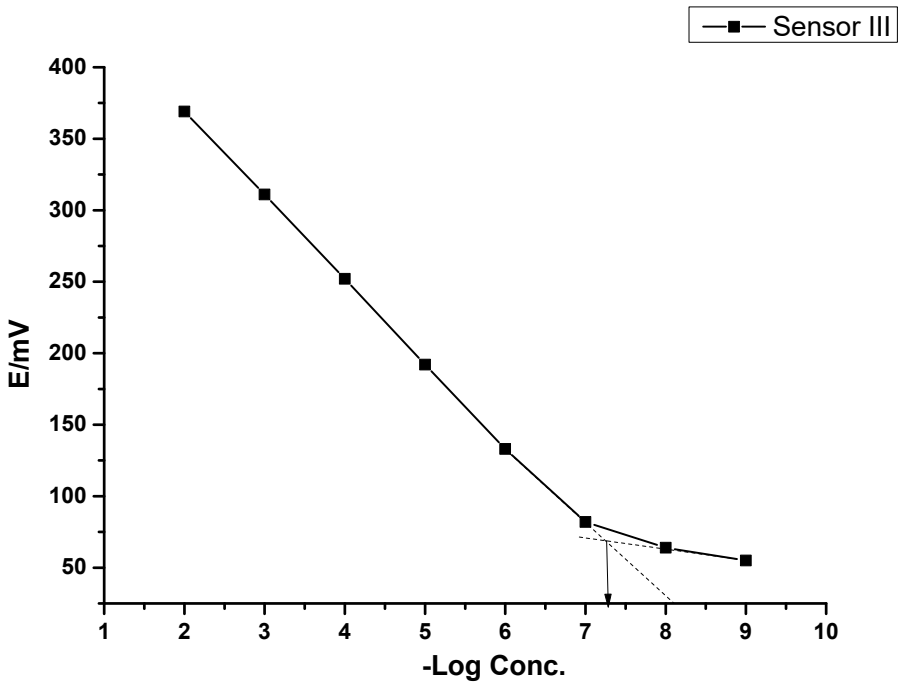

Figure S5 Showing calculation of LOD for CBZ by the proposed sensor III.